

**INK FOR PRINTING CONTACT LENSES, A PRINTING PROCESS FOR
COLOURED CONTACT LENSES, AND LENSES MADE THEREBY**

Field of Invention

This invention relates to an ink for use in the colouring of contact lenses, as well as a method for the colouring of contact lenses, and lenses produced thereby.

Background of the Invention

Over the years many attempts have been made to modify or change the appearance of the colour of eyes using coloured contact lenses, with varying degrees of success. Attempts to produce an opaque lens with a natural
10 appearance are disclosed in U.S. Patents. Nos. 3,536,386, (Spivak), 3,679,504 (Wichterle), 3,712,718 (LeGrand), 4,460,523 (Neefe), 4,719,657 (Bawa), 4,744,647, (Meshel et al.), 4,634,449 (Jenkins), European Patent Publication No. 0 309 154 (Allergen), 0472 496 A2 (Ciba-Geigy) and U.K. Patent Application No. 2 202 540A (IGEL).

Commercial success was achieved by the coloured contact lens described in U.S. Patent. No. 4,582,402 of Knapp. The Knapp colour contact lens was achieved by printing an intermittent pattern of opaque ink dots over the area of the contact lens that covers the iris. Various efforts have been made to improve
20 upon the success of the Knapp lens including those disclosed in U.S. Patent. No. 5,414,477 to Jahnke. Other examples of methods for producing coloured contact lenses are described in U.S. Patents. No. 5,018,849 (SU et al.), U.S.

Patent. No. 5,302,978 (Evan et al.), U.S. Patents. No. 5,120,121 (Rawlings et al.), and U.S. Patent. No. 5,166,122 (Rawlings).

For a colour binding and staining technique, U.S. Patent. No. 4,668,240 (Loshack) discloses a coloured contact lenses produced, in its preferred embodiment, from lens polymers and binding polymers containing the functional groups $-H$ and $-COOH$, and an additional compound containing at least two groups per molecule of the group $-NCO$ (isocyanate).

- 10 U.S. Patent. No. 4,857,072 (Narducy) discloses a colour binding mechanism that is different from that of Loshack, but which also, in its preferred embodiment, requires an isocyanate compound.

Although lenses produced in accordance with the Loshack and Narducy patents have been a commercial success, their manufacture requires use of an isocyanate compound for binding the colour to the lenses. The isocyanate compound has several disadvantages. Its vapors are noxious, and toxic, if inhaled. Thus it must be used with great caution. The isocyanate compound is chemically very reactive with active hydrogen groups such as $-OH$ in water molecules. Thus, its concentrations can be reduced, if such molecules are present in the production environment. Its great reactivity also gives rise to pot-life problems. After it is added to the colour coating ink, the viscosity increases rapidly to a point where the ink must be discarded. The changing viscosity makes control of the coating process difficult, and affects the quality of the coating. It has now been found that the arrangement fails to work in

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practice. For instance, when the diisocyanate compound is added to a printer's ink mixture having the generally known HEMA (hydroxyethyl methacrylate) bonding agent polymer, the compound reacts immediately with the bonding agent polymers, thus gelifying the mixture. This renders printing infeasible. Furthermore, isocyanates are substances highly harmful to human health, and therefore their use in a contact lens printing procedure involves a health risk.

U.S. Patent. No. 5,272,010 (Quinn) disclosed a process whereby one is not required to use an isocyanate compound as an adhesion promoter. U.S. Patent
10 No. 5713963 (Bensky) describes staining a contact lens consisting of a polymer containing hydroxyl and/or carboxyl groups, wherein part of the surface of the lens is coated with a colour coating containing, as a polyercross-linking agent, a compound with two urethane groups or a mixture of such compounds. Although they have several advantages over Loshaek's embodiment, the preparations of the bonding agent polymer, the cross-linking agent, and colour coating mix are complicated. Variations in the viscosity of the colour coating mix, and its bad fluidity, resulted in this process not being used in mass production. Furthermore its use lead to pattern colour inconsistency, and to an increase in the number of lenses rejected. All of this added to the cost of
20 producing coloured contact lens.

The object of the present invention is to address the problems of the prior art. More particularly, it is an object of the present invention to use a colour ink mixture containing acrylic pigmented polymer emulsion, and a co-solvent; as well as a procedure enabling convenient colouring of contact lenses, and by

which relatively firm adherence of the colour ink on the lens surface may be attained. A further object of the invention is to provide a dry lens printing and curing process which results in a coloured contact lens with a relatively natural appearance.

Producing a contact lens by polymerization and subsequent shaping is well known in the art and is not to be considered to be a part of the present invention.

10 Summary of the Invention

With the above and other objects in mind, the present invention provides a method for the printing of a contact lens constructed of a hydrophilic polymer, the method including the steps of:

- a) Providing an ink mixture including at least one acrylic pigmented polymer emulsion;
- b) Printing the ink mixture on to a dry lens surface of the contact lens;
- c) Subjecting the printed contact lens to predetermined temperature and atmospheric conditions for a predetermined time to cause the pigment to adhere to the lens.

Preferably, the ink mixture contains a solvent which contains one or more of the functional groups $-\text{CO}_2$, $-\text{CH}_2\text{CH}_3$ and $-\text{OH}$.

Preferably, the acrylic pigmented polymer emulsion is in the range of from 50 to 60% weight of the ink mixture, and the solvent is in the range of from 40 to 70% by weight of the ink mixture. The solvent may be ethyl lactate.

The contact lens may have an iris pattern printed thereon, preferably on a front, convex surface of the lens.

The predetermined temperature may be 120°C, and the predetermined time may be 12 hours.

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The method may further include the step of hydrating the lens in a saline solution for a required time, preferably in the range of from 2 to 5 hours. The saline solution may have a pH of 8.2 and may be at a temperature of 80°C. Preferably, the saline solution is stirred during the hydration.

In another aspect the present invention provides an ink mixture to be used to print a contact lens with a colour, the ink mixture including at least one acrylic pigmented polymer emulsion, and a solvent.

20 Brief Description of the Drawings

In order that the invention may be readily understood and put into practical effect, there shall now be described by way of non-limitative example only a preferred embodiment of the present invention, the description being with reference to the accompanying illustrative drawings in which:

FIG. 1 is a representation of a prior art product;

FIG. 2 illustrates the changes taking place in the colour ink mixture/lens system during the heating and hydration steps;

FIG. 3 is a representation corresponding to Fig. 1 but of a first form of the present invention;

FIG. 4 is an illustration corresponding to Figure 5 but of a second form of the present invention;

FIG. 5 is an illustration corresponding to Figures 5 and 6 but of a third form of the present invention;

FIG. 6 illustrates the UV-Vis spectra of a clear contact lens; and

FIG. 7 illustrates the UV-Vis spectra of a blue coloured contact lens, revealing the transmittance after printing a colour ink layer with dot/line pattern.

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Description of the Preferred Embodiments

This procedure is related to the preparation of inks for contact lenses substrates, which make up the lenses. Such lenses may also be called "cosmetic" lenses as they may modify the colour of the eyes. This may be achieved by suspending a mixture of acrylic polymer emulsion with a co-solvent such as, for example,

ethyl lactate ($\text{CH}_3\text{CH}(\text{OH})\text{COOC}_2\text{H}_5$) and applying the resultant mixture to one surface of the contact lens by transfer pad printing. The surface is preferably dry and, more preferably, is the front, convex surface.

The first aspect of present invention provides new reaction mechanisms and industrial implement.

The colour mixture and lens polymer are bonded to each other by the bonding of a first functional group, preferably selected from at least one of $-\text{COOH}$,
10 $-\text{OH}$, and $-\text{NH}$, with a second functional group, preferably of an ester $-\text{CH}(\text{OH})\text{CO}_2\text{-R}$, $\text{R} = \text{CH}_3$ or C_2H_5 and an acid. By heating and hydration strong hydrogen bonding and covalent bonds are formed. FIG. 2 illustrates the changes taking place in the colour ink mixture/lens systems during heating and hydration and shows the surface of the lens 1; functional groups 2, 3; hydrogen bonds 4; and covalent bonds 5.

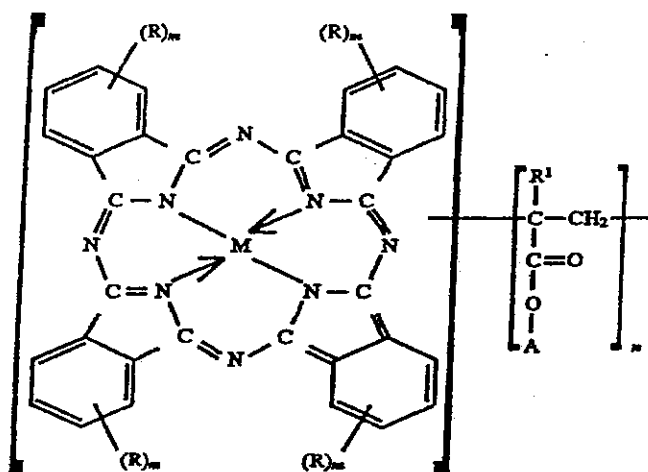
An acrylic polymer emulsion of a pigment can be used provided the pigment can be dissolved in the solvent used to prepared the binding ink mixture, and which provides the proper physical and technical properties for printing. The
20 pigments chosen must contain certain functional groups, and a listing of preferred pigments is shown in Table 1.

Color	Chemical name
Cadmium Yellow Orange	Cadmium Sulfo-Selenide
Yellow Ochre	Hydrous Iron Oxide
Middle Green	Monoazo, Polychloro Copper phthalocyanine
Acanthus Green	Anhydrous Chromium Sesquioxide
Cerulean Blue	Cobalt Stannate
Compose Blue #2	Copper phthalocyanine, Titanium Dioxide
Compose Violet	Dioxazine Pigment, Titanium Dioxide
Light Brown	Condensed Azo Pigment
Mars Black	Ferroso-Ferric Oxide
Titanium White	Titanium Dioxide
Grey V-7	Carbon, Hydrous Iron Oxide, Titanium Dioxide
Grey V-5	Titanium Dioxide, Hydrous Iron Oxide, Carbon

TABLE 1

Blends of different colouring substances may be used to achieve the desired performance. For example, the poly(meth)acrylate combined methallophthalocyanine compound has a structure in which a methallophthalocynine group and a (meth)acrylic acid copolymer moiety are combined with each other.

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The various compounds used in the colour mixture, including the pigment binding and solvent compounds, depend on an acid-based catalyst which differs from that of the isocyanate compounds of the prior art. Isocyanate compounds are very reactive with even trace amounts of water or alcohol. The compounds of the present invention are generally stable when water or alcohol are present. This stability permits greater control of reaction speed, and a wider range of compatibility. These present problems with isocyanate compounds. The result is a greater control of pot life, and viscosity variation, which can translate into improved product quality.

According to one embodiment of the invention the colour coating formulation is provided in the form of a mix with one step. The viscosity of the mix is advantageously adjusted by addition of a co-solvent appropriate for the coating method employed. The colour coating formulation is advantageously imprinted in a known manner directly on the front, convex lens surface to give a configuration simulating the structure of the iris.

Preparation Of Ink Mixture Usable In Printing:

10	Co-solvent	100.0g
	Catalyst	0.2g
	Colour substance	quantity desired

The components are mixed. The viscosity can be adjusted by addition of a solvent, if needed. The quantities of colour substance to be used varies in accordance with the colour substance(s) used, and the completed effect desired.

The co-solvent may be any suitable compound such as, for example, ethyl lactate; the catalyst can be of a suitable form such as, for example,
 20 amineonacid.

Although the exact shades used in practising the invention are not critical, the shades produced by the inks shown in the Table 2 below are presently preferred:

TABLE 2

No.	Nominal Colour	Cd ₂ SeS	Feo	PCP	Cr ₂ O ₃	CoP	TiO ₂	DP	FFO	C	CP	CCA
1	Grey		x				x		x	x		
2	Green			x	x							
3	Violet						x	x				
4	Blue					x					x	
5	Aqua			x			x				x	x
6	Chesnut	x					x		x			
7	Hazel	x	x				x		x			

In the above table, the following abbreviations are used:

Cd ₂ SeS	Cadmium Sulfo-Selenide
FeO	Hydrous Iron Oxide
PCP	Polychroero Copper Phthalocyanine
Cr ₂ O ₃	Anhydrous Chromium Sesquioxide
CoP	Copper Phthalocyanine
TiO ₂	Titanium Dioxide
C	Carbon
CCA	Cobalt-Chromium Aluminate
FFO	Ferroso-Ferric Oxide

Lens Printing Procedure:

A contact lenses in accordance with the disclosure in Knapp's U.S. Patent. No. 4,582,402 is illustrated in FIG. 1. The elements of the pattern is made-up of a series of dots, and especially preferred are dots where some of them run together. The lense is printed, i.e. a type of coating, with a coloured dot pattern in accordance with U.S. Pat. No. 4,582,402 (Knapp). For each ink and lens, the ink is placed on a metal cliché containing an image formed by a pattern of recessed cells. Excess ink is removed from the cliché by wiping the surface with a doctor blade. Ink in the recessed image is removed by transferring it to
10 a soft rubber pad, which is pressed over the recessed image. Ink on the rubber pad is then transferred to a lens by contacting the inked part of the pad with the lens. Freshly printed lenses are heated up 12 hours at 120°C to complete the bonding and processes.

This aspect of the invention may be summarized as a method for making a coloured contact lens including the steps of:

- 1) the printing of dry contact lensesly:
 - a) setting up an ink cup pad printing machine ;
 - 20 b) placing the lens onto the chuck and centrally aligned is within the guide ring;
 - c) standing the vacuum pump to hold the lens in position;
 - d) applying the ink mixture on the cliché using a brush ensuring that the mixture covers the "iris pattern";
 - e) removing the excess ink mixture on the cliché by a doctor blade;

- f) applying the pad to the cliché for it to pick up the ink mixture;
 - g) moving the pad forwards;
 - h) moving the pad vertically to transfer the ink mixture on to the lens;
 - i) moving the pad backwards;
 - j) stopping the vacuum pump to release the lens; and
 - k) removal of the lens from the chuck and placing it on a tray.
- 2) the fixing of the colour coating on the lens surfaces by heating the lens in an oven so that bonding takes place and the bond, as well as the ink mixture, is cured. A preferred temperature is about 120°C, for a preferred duration of about 12 hrs. However, other temperatures and durations may be used to give the same effect. Excessive temperatures should be avoided to reduce the likelihood of damage to the lens.
- 3) and finally, the hydration of the coated lenses:
- Upon the heat treatment concluding, the dry lens is placed in a basket (preferably of a plastics material) and is immersed in a buffered saline solution preferably with a pH of 8.2. The solution is stirred at a temperature of about 70° to 80° C for a duration of about 2 to 2.5 hrs.
- Water is thereby absorbed into the lens from the solution and the solution dissolves potential non-reacted components that are left in or on the lens.

Spectral Transmittance and Adhesion Testing:

The colourants used in the ink mixture are listed in Table 1. For example, for a hazel colour, homogeneously mix 1.000g of acrylic pigmented polymer

emulsion, including Cadmium Sulfo-Selenide, and hydrous Iron Oxide, Titanium Dioxide and Ferroso-Ferric Oxide, with 0.7000g of a co-solvent to form a printing ink mixture.

A dry disposable lens is printed on its front, convex side with ink of a shade containing pigment, and a binding solvent. The printed pattern is shown in Figure 2. It covers most of the iris section, having an annular form, with an outer radius R' of about 6.25mm and an inner radius R'' of about 3.05mm.

- 10 The printed disposable colour lens is then placed in a petri dish and placed in an oven. The temperature in the oven is maintained relatively constant at about 120°C for about 12 hours. The petri dish is then removed, put aside to cool to room temperature, and the lens taken for hydration.

The special transmittance curves of clear lens and blue coloured lens were measured according to the ISO wet cell method in the wavelength 200 to 800 nm. Both curves, Fig. 6 for clear lens and Fig. 7 for blue coloured lens, show about 90% transmittance. It means that the colour printing pattern on lens does not affect the light transmittance.

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Hydrated coloured lenses were examined to determine if any printed pattern was removed by rubbing with finger, and cleaning it in ultrasonic cleaner for 5 minutes. The result shows that the colour adhesion is satisfactory for normal use.

Whilst there has been described in the foregoing description preferred embodiments of the present invention, it will be understood by those skilled in the technology that many variations or modifications in specific details may be made without departing from the present invention.

CLAIMS

1. A method for printing a contact lens constructed of a hydrophilic polymer, the method including steps of:

- 5 (a) providing an ink including at least one acrylic pigmented polymer emulsion and a co-solvent;
- (b) printing the ink on to a dry lens surface of the contact lens;
- (c) subjecting the printed contact lens to temperature and atmospheric conditions for a predetermined time to cause the pigment to adhere
- 10 to the lens;

wherein the acrylic pigmented polymer emulsion is in the range of from 50 to 60% by weight of the ink.

2. The method of claim 1, wherein the co-solvent has one or more of the

15 functional groups —CO_2 , $\text{—CH}_2\text{CH}_3$ and —OH .

3. The method of claim 2, wherein the solvent is in the range of from 40 to 70% by weight of the ink.

20 4. The method of claim 2 or claim 3, wherein the solvent is ethyl lactate.

5. The method of any one of claims 1 to 4 wherein the contact lens has an iris pattern printed thereon.

25 6. The method of any one of claims 1 to 5, wherein the surface is a front, convex surface of the lens.

7. The method of any of claims 1 to 6, wherein the temperature is 120°C .

30 8. The method of any one of claims 1 to 7, wherein the predetermined time is 12 hours.

9. The method of any one of claims 1 to 8, including the further step of hydrating the lens in a buffered saline solution for a required time.

5 10. The method of claim 9, wherein the required time is in the range of from 2 to 5 hours.

11. The method of claim 9 or claim 10, wherein the buffered solution has a pH of 8.2.

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12. The method of any one of claims 9 to 11, wherein the saline solution is at a temperature of 80°C.

13. The method of any one of claims 9 to 12, wherein the saline solution is
15 stirred during the hydration.

14. The method of any one of claims 1 to 13, wherein the surface is dry.

15. An ink to be used to print a contact lens of an hydrophilic polymer with a
20 colour, the ink including at least one acrylic pigmented polymer emulsion, and a solvent containing one or more of the functional groups $-\text{CO}_2$, $-\text{CH}_2\text{CH}_3$ and $-\text{OH}$, the acrylic pigmented polymer emulsion is in the range of from 50 to 60% weight of the ink mixture.

25 16. An ink as claimed in claim 15, wherein the solvent is in the range of from 40 to 70% by weight of the ink mixture.

17. An ink as claimed in any one of claims 15 to 16, wherein the solvent is ethyl lactate.

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18. A contact lens construct of a hydrophilic polymer when printed according to the method of any one of claims 1 to 14.
19. A contact lens constructed of a hydrophilic polymer when printed with the
5 ink of any one of claims 15 to 17.